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(54) Abstract Title

Preparation of a catalyst

(57) A process for preparing a catalyst comprising at least one support, at least one metal from group VIII of the periodic table and at least one additional element M selected from the group formed by germanium, tin, lead, rhenium, niobium, gallium, indium and thallium is described, in which said element M is introduced in an aqueous solvent at a pH of less than 10, in the form of at least one hydrosoluble organometallic compound comprising at least one carbon-M bond. Also disclosed is a catalyst obtained using the process and the use of the catalyst in organic compound transformation reactions, such as dehydrogenation and hydroreforming.

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PREPARATION OF A CATALYST

The present invention relates to a novel process for preparing a catalyst comprising at least one support, at least one binder, at least one metal from group VIII of the periodic table (Handbook of Physics and Chemistry, 63rd edition, 1982-83) and at least one additional element M selected from germanium, tin, lead, rhenium, niobium, gallium, indium, thallium, gold and silver. This catalyst can also contain at least one other element selected from alkali metals and/or a metalloid such as sulphur and/or any other chemical element such as a halogen or a halogenated compound. The invention also relates to a catalyst obtained using the process of the present invention and to its use in reactions for transforming organic compounds such as hydrocarbons.

Many patents and publications have demonstrated that the addition of promoters to a base metal improves the quality of the catalysts. Such elements are added in different forms such as salts or organometallic compounds. In general, more active or more selective catalysts are obtained, which are sometimes more stable than the corresponding monometallic catalyst. The manner of introducing such modifiers is important as it strongly influences the properties of the catalyst.

A great deal of work has been carried out on formulations for catalysts used in hydrocarbon conversion processes, in particular that of catalytic reforming and selective hydrogenation. They are acid catalysts comprising a noble metal from the platinum family and at least one additional metal M such as tin, germanium, lead, rhenium, gallium, indium, gold and silver in addition to a support. They have been described in United States patent US-A-3 998 900 and French patent FR-A-2 495 605. These catalysts are bifunctional as they combine two functions which are essential for producing the proper performance: a hydrodehydrogenating function

which dehydrogenates naphthenes and hydrogenates coke precursors, and an acid function which isomerises the naphthenes and paraffin, and cyclises long chain paraffins. Platinum has a hydrogenolysing activity to the detriment of the gasoline and/or aromatic compound yields desired for catalytic reforming or in the aromatic compound production process. Such a hydrogenolysing activity can be substantially reduced, and the selectivity thus increased, by adding an additional metal M. Further, adding this element M can also increase the hydrogenating properties of the platinum, which encourages hydrogenation of coke precursors and thus the stability of the catalyst. The performance of such bimetallic catalysts as regards activity and/or selectivity is better than that of catalysts containing only the principal metal (palladium, platinum or nickel). The metals in the catalyst are added in different forms such as mineral salts or organometallic compounds. The manner in which such modifiers are introduced is important as it strongly influences the properties of the catalyst. Thus the additional metal M is advantageously introduced using an organometallic compound of said metal M. This technique of introducing metal M has been described in the Applicant's United States patent US-A-4 548 918 and in US-A-3 531 543.

US-A-5 128 300 describes the preparation of a catalyst by peptising an inorganic oxide with introduction of a group IVA metal in the form of a halogenated organic compound.

The processes cited above describe the production of a catalyst by using at least one organometallic compound of element M. Element M is introduced in the form of at least one organometallic compound selected from the group formed by complexes, in particular carbonyl complexes, polyketone complexes of metals M and metal hydrocarbyls of element M such as alkyls, cycloalkyls, aryls, metal alkylaryls

and metal arylalkyls. US-A-4 727 216 describes the preparation of dehydrogenation catalysts using organometallic tin compounds such as halogenated organometallic tin compounds.

Introducing additional element M in the form of an organometallic compound
5 leads to catalysts with better performances but necessitates the use of an organic solvent. The impregnation solvent described in US-A-4 548 918 is selected from the group formed by oxygen-containing organic solvents containing 2 to 8 carbon atoms per molecule, paraffinic, naphthenic or aromatic hydrocarbons essentially containing 6 to 15 carbon atoms per molecule, and organic compounds and halogenated oxygen-
10 containing compounds containing 1 to 15 carbon atoms per molecule. Such solvents can be used alone or as a mixture.

The Applicant's French patent applications FR 97/13684, FR 97/13685, FR 97/13686 and FR 97/13687 describe introducing the additional element M in the form of a hydrosoluble organometallic compound of element M in an aqueous
15 solvent and the use of the catalyst thus prepared for paraffin dehydrogenation, hydroreforming and selective hydrogenation of unsaturated compounds.

We have now discovered that the element M can be introduced in an aqueous solvent at a pH of less than 10. Thus the present invention provides a novel process for preparing a catalyst comprising at least one support, at least one metal from group
20 VIII of the periodic table and at least one additional element M formed by germanium, tin, lead, rhenium, niobium, gallium, indium, thallium, gold and silver, characterized in that said additional element M is introduced in the form of at least one organometallic compound comprising at least one carbon-M bond in an aqueous solvent at a pH of less than 10. The present invention also concerns the use of a
25 catalyst prepared using the process of the invention in a process for hydrogenating

unsaturated compounds and in a process for catalytic hydroreforming and aromatic compound production.

The invention represents a substantial advance in facilitating the manufacture of the catalyst. Using industrial quantities of organic solvents has substantial disadvantages as regards safety (flammability, toxicity) and as regards costs. Further, the solubility of organometallic compounds of element M is substantially improved in solutions with a pH in the range 0 to 10, which means that much smaller quantities of solvent can be used compared with prior art processes.

Various preferred features and embodiments of the present invention will now be described by way of non-limiting example.

The catalyst prepared using the process of the invention comprises at least one support. The support comprises at least one refractory oxide which is generally selected from oxides of metals from groups IIA, IIIA, IIIB, IVA or IVB of the periodic table such as magnesium, aluminium, silicon, titanium, zirconium or thorium oxides used alone or as a mixture or mixed with oxides of other elements from the periodic table. Charcoal can also be used.

For hydrocarbon transformation reactions, the preferred support is alumina with a specific surface area which is advantageously in the range 5 to 400 m² per gram, preferably in the range 50 to 350 m² per gram. It is also possible to use X, Y, mordenite, faujasite, ZSM-5, ZSM-4, ZSM-8, MFI, EUO or mazzite type zeolites or molecular sieves as the support, as well as mixtures of oxides of metals from groups IIA, IIIA, IIIB, IVA and IVB with the zeolitic material, in particular aluminium oxide-zeolite mixtures. Preferred supports used in transforming organic functions are silica, charcoal and alumina.

In addition to the support, the catalyst of the invention comprises:

- a) at least one group VIII metal selected from iridium, nickel, palladium, platinum, rhodium and ruthenium. Platinum and palladium are the preferred metals for hydrocarbon conversion reactions. Rhodium and ruthenium are preferred metals for transforming functional molecules. The percentage by weight with respect to the total catalyst weight is, for example, in the range 0.01% to 10%, preferably in the range 0.05% to 5%. Palladium, nickel and platinum are the preferred metals for selective hydrogenation of unsaturated compounds. The percentage by weight with respect to the total catalyst weight is then in the range 0.01% to 50%, preferably in the range 0.05% to 1% if the metal is a noble metal and in the range 5% to 30% if the metal is nickel. Platinum and iridium are the preferred metals for hydroreforming. The percentage by weight is then in the range 0.01% to 10%, preferably in the range 0.05% to 5%; and
- b) at least one additional element M selected from germanium, tin, lead, rhenium, niobium, gallium, indium, thallium, gold and silver introduced in the form of an organometallic compound in an aqueous solvent at a pH in the range 0 to 10. Tin, germanium, silver and gold are the preferred elements for selective hydrogenation of unsaturated compounds. Tin and germanium are the preferred elements for hydroreforming. The percentage by weight with respect to the total catalyst weight is, for example, in the range 0.01% to 10%, preferably in the range 0.02% to 5%. In some cases it may be advantageous to use at least two of the elements from this group each introduced in the form of an organometallic compound.

Depending on the field of application, the catalyst can optionally also contain, for example, 0.1% to 3% by weight of a halogen or a halogenated compound. It can

also contain 0.1% to 3% by weight of an alkali or alkaline-earth metal. It can also optionally contain 0.01% to 2% by weight of an element such as sulphur. It can also contain 0.01% to 3% by weight of at least one other element M which can be introduced into the catalyst using any method and in any of the forms which are
 5 known to the skilled person.

Non limiting examples of the precursor of element M include those selected from halogenated compounds, hydroxides, oxides, carbonates, carboxylates, nitrates and sulphates of organometallic compounds of element M. These compounds comprise at least one carbon-M bond. As an example, the precursor of element M
 10 can be selected from polyalkyl halides, for example trimethyl halides (Me_3MX), triethyl halides, (Et_3MX), dimethyl dihalides (Me_2MX_2), diethyl dihalides (Et_2MX_2), diisopropyl dihalides (iPr_2MX_2), di-n-propyl dihalides ($\text{n-Pr}_2\text{MX}_2$), methyl trihalides (MeMX_3), ethyl trihalides (EtMX_3), isopropyl trihalides (iPrMX_3), n-propyl trihalides (n-PrMX_3), polyalkyl hydroxides, for example trimethyl hydroxides
 15 (Me_3MOH), triethyl hydroxides (Et_3MOH), dimethyl dihydroxides ($\text{Me}_2\text{M}(\text{OH})_2$), diethyl dihydroxides ($\text{Et}_2\text{M}(\text{OH})_2$), diisopropyl dihydroxides ($\text{iPr}_2\text{M}(\text{OH})_2$), di-n-propyl dihydroxides ($\text{n-Pr}_2\text{M}(\text{OH})_2$), methyl trihydroxides ($\text{MeM}(\text{OH})_3$), ethyl trihydroxides ($\text{EtM}(\text{OH})_3$), isopropyl trihydroxides ($\text{iPrM}(\text{OH})_3$), n-propyl trihydroxides ($\text{n-PrM}(\text{OH})_3$), polyalkyl acetates, for example trimethyl acetates
 20 ($\text{Me}_3\text{MOC}(\text{O})\text{Me}$), triethyl acetates ($\text{Et}_3\text{MOC}(\text{O})\text{Me}$), tributyl acetates ($\text{Bu}_3\text{MOC}(\text{O})\text{Me}$), polyalkyl oxides, for example bis trimethyl oxides ($[\text{Me}_3\text{M}]_2\text{O}$), bis triethyl oxides ($[\text{Et}_3\text{M}]_2\text{O}$), bis tripropyl oxides ($[\text{Pr}_3\text{M}]_2\text{O}$), bis tributyl oxides ($[\text{Bu}_3\text{M}]_2\text{O}$), polyalkyl sulphates, for example bis trimethyl sulphates ($[\text{Me}_3\text{M}]_2\text{SO}_4$), bis dimethyl sulphates ($[\text{Me}_2\text{M}]\text{SO}_4$), methyl-trioxo sulphates (MeMO_3), where X
 25 represents a halogen selected from fluorine, chlorine, bromine and iodine. The

precursor of element M can also be selected from compounds with general formula $(R1)_xM(R2)_y(R3)_z$ where $x+y+z$ = the valency of metal M and where R1 is selected from alkyl, cycloalkyl, nitrile (CN), carbonyl (CO), aryl, alkylaryl and arylalkyl radicals, where R2 is a function with formula $C_aH_bR'_c$, where R' represents a
 5 hydroxide, halide, carboxylate, PO_3H or SO_3H function and where R3 is an aquo, oxo (MO), alkoxide (o-alkyl), hydride, hydroxyl, alkylsulphonate, alkylsulphate, thioalkyl, $N(SO_3R'')_2$, PR''_2 or PR''_3 group where R'' is an alkyl group and P represents phosphorus (Handbook of Physics and Chemistry, 63rd edition, 1982-83).

The term "alkyl groups" means saturated, linear, branched or cyclic groups
 10 containing carbon and hydrogen atoms. The term "aryl groups" means aromatic groups.

At least one alkyl group in the precursors defined above can also be replaced by an alkenyl group, i.e., an unsaturated, linear, branched or cyclic group containing carbon and hydrogen atoms, for example an allyl group.

15 When the metal M is tin, preferred precursors are polyalkyl halides such as Me_3SnCl , Me_2SnCl_2 , $MeSnCl_3$, Et_3SnCl , Et_2SnCl_2 , $EtSnCl_3$, $iPrSnCl_2$ and the hydroxides Me_3SnOH , $Me_2Sn(OH)_2$, Et_3SnOH , $Et_2Sn(OH)_2$, the oxide $[Bu_3Sn]_2O$, and the acetate $Bu_3SnOC(O)Me$.

When metal M is germanium, the preferred precursor is the oxide
 20 $[EtGeO]_2O$.

When metal M is niobium, preferred precursors are niobium bis-cyclopentadienyl hydroxy bromide $p(C_5H_5)_2Nb(OH)Br_2$, niobium bis-cyclopentadienyl hydroxy dichloride $(C_5H_5)_2Nb(OH)Cl_2$, niobium bis-cyclopentadienyl tribromide $(C_5H_5)_2NbBr_3$ and niobium bis-cyclopentadienyl
 25 trichloride $(C_5H_5)_2NbCl_3$.

When metal M is rhenium, the preferred precursor is methyl trioxorhenium MeReO_3 .

When metal M is lead, preferred precursors are the halides Me_2PbCl_2 , Et_2PbCl_2 and the hydroxides $\text{Et}_2\text{Pb}(\text{OH})_2$ and $\text{Me}_2\text{Pb}(\text{OH})_2$.

5 In accordance with the preparation process of the present invention, the group VIII metal, additional metal M in the organometallic form, optional halogen or halogenated compound, optional alkali or alkaline-earth metal, optional metalloid, and optional other metal M can be introduced simultaneously or successively in any order.

10 In accordance with the invention, contact with the organometallic element M is characterized in that element M is introduced in an aqueous solvent. The pH of the solution containing element M is in the range 0 to 10. Preferably, the value of the pH is strictly less than 10. The other elements can be introduced using any method known to the skilled person.

15 In one method of the invention, additional metal M can be introduced during synthesis of the support using a sol-gel type technique. As an example, for a support containing alumina and/or silica, a mixed metal M-alumina and/or metal M-silica gel can be obtained by hydrolysing an organic solution of $\text{Al}(\text{OR}')_3$ or $\text{Si}(\text{OR}')_4$ in a solvent such as ROH with an aqueous solution, at a pH in the range 0 to 10, of an organometallic compound of element M. R and R' designate a methyl, ethyl, isopropyl, n-propyl or butyl type alkyl group or even a heavier group such as n-hexyl. The alcoholic solvent must be intensely dehydrated before introducing the aluminium alcoholate and/or the silicon alcoholate. After hydrolysis, heat treatment of the gel obtained carried out at a temperature in the range 200°C to 800°C, 20 preferably in the range 300°C to 700°C, more preferably in the range 400°C to 25

500°C, can ensure complete reaction of the hydrosoluble organometallic compound of element M with the gel, which causes formation of the mixed oxide $\text{Al}_2\text{O}_3\text{-MO}_x$ and/or $\text{SiO}_2\text{-MO}_x$.

In a further method, element M can be added to an alumina sol.
5 US-A-3 929 683 describes the introduction of tin in the form of a salt, for example SnCl_2 into an alumina sol. In accordance with the present invention, it is possible to add an organometallic compound of element M in an aqueous solvent at a pH in the range 0 to 10 to an alumina hydrosol, said alumina hydrosol being obtained, for example, by precipitating an acidic AlCl_3 solution at a pH of 4-5 then encouraging
10 the reaction of the compound of element M with the alumina hydrosol, for example using heat or a base.

In a further implementation of the invention, additional element M can be introduced during production of the support using prior art support forming techniques such as extrusion (US-A-3 917 808) or oil drop (US-A-3 558 508).

15 When preparing the catalyst of the invention by the oil drop method, preferred hydrosoluble organometallic precursors of element M are selected from oxide or carboxylate compounds, for example of tin such as tributyl tin bis oxide compounds or tributyl tin carboxylates. An aqueous solution of at least one compound of element M, with a pH of less than 10, is directly introduced into the
20 alumina suspension before forming it by the oil drop method or by extrusion. This compound is then dried and calcined in air between 350°C and 700°C. The oxide support containing the element M obtained is then impregnated using an aqueous or organic solution of at least one compound of a group VIII metal, the volume of the solution preferably being in excess with respect to the retention volume of the
25 support, or equal to this volume. After leaving in contact for several hours, the

product obtained is dried and calcined in air between 300°C and 600°C, preferably in a stream of air for several hours. In a further variation, it is also possible to introduce at least one hydrosoluble organometallic compound of metal M and at least one compound of a group VIII metal simultaneously during the support forming step.

In this particular implementation, preferred precursors of element M are selected from polyalkyl acetates, polyalkyl oxides, polyalkyl carbonates, polyalkyl carbonates, polyalkyl sulphates, compounds with general formula $(R1)_xM(R2)_y(R3)_z$ where $x+y+z$ = the valency of metal M and where R1 is selected from the group formed by alkyl, cycloalkyl, nitrile (CN), carbonyl (CO), aryl, alkylaryl and arylalkyl functions, where R2 is a function with formula $C_aH_bR'_c$, where R' represents a hydroxyide, carboxylate, PO_3H or SO_3H function and where R3 is an aquo, oxo (MO), alkoxide (O-alkyl), hydride, hydroxyl, alkylsulphonate, alkylsulphate, thioalkyl, $N(SO_3R'')_2$, PR''_2 or PR''_3 group where R'' is an alkyl group.

As an example, it is possible to mill the moist powder acting as a support with the catalyst precursors then to form, dry and calcine it.

In a further method, the catalyst can be prepared using different procedures for impregnating element M and the invention is not limited to a set impregnation procedure. When a number of solutions are used, intermediate drying and/or calcining steps can be carried out.

In a preferred technique of the invention, the catalyst is obtained by impregnating the support using at least one aqueous or organic solution of at least one compound of at least one group VIII metal. The impregnated support is then filtered, optionally washed with distilled water and dried. It is then reduced in hydrogen at a temperature which is normally in the range about 200°C to about

600°C and preferably in the range about 300°C to about 500°C. There may be an intermediate calcining step carried out in air between the drying and reduction step. The product obtained is then impregnated with an aqueous solution of at least one compound of tin, germanium, lead, rhenium, niobium, gallium, indium or thallium.

5 The volume of the aqueous solution is equal to the retention volume of the support and is preferably in excess with respect to this volume. The pH of the aqueous solution is in the range 0 to 10. After leaving the support impregnated with the group VIII metal in contact with the aqueous solution containing at least one compound of element M, for example for several minutes to several hours, the
10 product is filtered, optionally washed with water and dried. This method is terminated by reduction between 300°C and 600°C, preferably in a stream of hydrogen for several hours. After the drying step, it is also possible to finish by calcining between 300°C and 600°C in a stream of air.

In a further technique in accordance with the invention, element M is
15 impregnated before introducing the group VIII metal. Thus the catalyst is obtained by impregnating a support using an aqueous solution of at least one organometallic compound of said element M, the volume of the solution being equal to the retention volume of the support or in excess with respect to that volume. Particularly advantageously, an aqueous solution of a halogenated organometallic compound of
20 element M is used such as Me_3MX or Me_2MX_2 where X represents a halogen such as chlorine or bromine, for example Me_3SnCl or Me_2SnCl_2 or an oxide of element M such as the tributyl bis oxide of element M, for example tributyltin bis oxide. The pH of the solution is in the range 0 to 10. After leaving the solid and impregnation solution in contact for several hours, the product is optionally dried then calcined
25 between 300°C and 600°C, preferably by flushing with air for several hours. The

solid obtained is then impregnated using an aqueous or organic solution of at least one group VIII metal compound, the volume of the solution being in excess with respect to the retention volume of the support or equal to that volume. After several hours contact, the product obtained is dried then calcined in air between 300°C and 600°C, preferably by flushing with air for several hours.

In a further implementation of the invention, element M and the group VIII metal can be introduced simultaneously during a step for impregnating a support with an aqueous solution comprising at least one element M and at least one group VIII metal, the volume of the solution being equal to the retention volume of the support or in excess with respect to that volume. Particularly advantageously, an aqueous solution of a halogenated organometallic compound of element M is used, such as Me_3MX or Me_2MX_2 , where X represents a halogen such as chlorine, for example Me_3SnCl or Me_2SnCl_2 or an oxide of element M such as the tributyl bis oxide of element M, for example tributyl tin bis oxide. The pH of the solution is in the range 0 to 10. The catalyst is then dried and heat activated, for example using one of the procedures described above.

Before use, the catalyst is reduced in hydrogen, for example between 20°C and 600°C, to obtain an active metallic phase. The procedure for this treatment consists, for example, of slowly raising the temperature to the maximum reduction temperature in a stream of hydrogen, for example in the range 20°C to 600°C, preferably in the range 90°C to 500°C, followed by keeping it at that temperature, for example for 1 to 6 hours.

This reduction can be carried out immediately after calcining or later with the user. It is also possible to directly reduce the dried product with the user.

It is also possible to carry out prior reduction of the group VIII metal compound in solution using organic molecules with a reducing nature, such as formic acid. The compound of the additional metal M can be introduced simultaneously or successively. The catalyst then be directly used when the catalytic
5 reaction requires an aqueous solvent, which is of particular application when transforming organic functions. A further possibility consists of filtering then drying the catalyst obtained. It can then be calcined and reduced under the conditions described above. It is also possible to carry out the reduction directly from the dried product.

10 When the catalyst of the present invention contains sulphur, the sulphur is introduced into the formed, calcined catalyst containing the metal or metals cited above, either *in situ* before the catalytic reaction or *ex situ*. Optional sulphurisation is carried out after reduction. With *in situ* sulphurisation, if the catalyst has not already been reduced, reduction is carried out before sulphurisation. With *ex-situ*
15 sulphurisation, reduction then sulphurisation is carried out. Sulphurisation is carried out in the presence of hydrogen using any sulphurising agent which is well known to the skilled person, such as dimethyl sulphide or hydrogen sulphide. As an example, the catalyst is treated with a feed containing dimethyl sulphide in the presence of hydrogen, with a concentration such that the sulphur/metal atomic ratio is 1.5. The
20 catalyst is then kept at about 400°C in a stream of hydrogen for about 3 hours before injecting the feed.

The catalyst prepared in accordance with the invention can be used in a process for transforming hydrocarbons used in the refining and petrochemicals fields. It can also be used in a process if the chemical field.

As an example, the catalyst prepared in accordance with the invention can be used in a process for dehydrogenating saturated aliphatic hydrocarbons and in particular a process for dehydrogenating C_3 - C_{22} paraffins. Light paraffin dehydrogenating processes can be used to upgrade aliphatic hydrocarbons with a low boiling point such as butanes and isobutanes, pentanes and isopentanes which can be recovered after extracting the unsaturated compounds from steam cracking or catalytic cracking cuts. The process for dehydrogenating longer chain paraffins is an important commercial process because of the current demand for mono-olefins for preparing biodegradable detergents or pharmaceutical products, for example.

When using the catalyst of the invention in the paraffin dehydrogenation process, metal M is preferably selected from germanium and tin and the metal from group VIII is preferably selected from platinum and palladium.

These different processes are distinguished from each other by the choice of operating conditions and the composition of the feed. The operating conditions are adjusted as a function of the nature of the feed to be treated to obtain the best pressure-temperature-yield and activity combination in a manner which is known to the skilled person. The dehydrogenation reaction is generally carried out at a pressure in the range 0.02 to 2 MPa, preferably in the range 0.1 to 1 MPa and at a temperature in the range 400°C to 800°C as a function of the nature of the feed.

The temperature is advantageously in the range 400°C to 550°C for a feed essentially comprising isopentane. The temperature is advantageously in the range 450°C to 550°C for a feed comprising principally paraffins containing 9 to 22 carbon atoms per molecule. The feed can also contain unsaturated hydrocarbons containing 3 to 22 carbon atoms per molecule. The mass flow rate of the treated feed per unit mass of catalyst is generally in the range 0.5 to 100 kg/kg/h. It may be advantageous

to use hydrogen as the diluent. The hydrogen/hydrocarbon mole ratio is generally in the range 0 to 20, preferably in the range 0 to 6.

In accordance with the invention, the catalyst described above is also advantageously used in processes for selective hydrogenation of cuts containing acetylenic compounds or dienes. The selective hydrogenation processes can eliminate the highly unsaturated compounds present in cuts from catalytic, thermal or steam cracking to upgrade these cuts either as polymerisation feeds or as a product which can be used as a base for an automobile fuel.

Typical feeds to be treated are C2, C3 or C4 steam cracking feeds; steam cracking cuts, and C3, C4 or C5 catalytic cracking gasolines. The feed is generally brought into contact with the catalyst of the present invention at a temperature in the range 20°C to 200°C. The mass flow rate of the treated feed per unit mass of catalyst can be between 0.1 and 10 kg/kg/h. The operating pressure can be set between atmospheric pressure and 6 MPa.

In accordance with the invention, the catalyst described above can also be used in processes for reforming gasoline and for the production of aromatic compounds. The reforming processes can increase the octane number of gasoline fractions originating from distilling crude oil and/or from other refining processes. Processes for producing aromatic compounds produce bases (benzene, toluene and xylenes) which can be used in the petrochemicals industry. These processes have a supplemental importance by contributing to the production of large quantities of hydrogen which are vital to hydrogenation and hydrotreatment processes carried out at the refinery. These two processes are distinguished by the choice of operating conditions and the composition of the feed.

A typical feed treated by these processes contains paraffinic, naphthenic and aromatic compounds containing 5 to 12 carbon atoms per molecule. This feed is defined, inter alia, by its density and its composition by weight. This feed is brought into contact with the catalyst of the present invention at a temperature in the range 400°C to 700°C. The mass flow rate of the treated feed per unit mass of catalyst can be in the range 0.1 to 10 kg/kg/h. The operating pressure can be set between atmospheric pressure and 4 MPa. A portion of the hydrogen produced is recycled in a molar recycle ratio in the range 0.1 to 10. This ratio is the molar ratio between the recycled hydrogen flow rate and the feed flow rate.

The following examples illustrate the invention without in any way limiting its scope.

A. PREPARATION OF CATALYSTS AND THEIR USE IN DEHYDROGENATING PARAFFINS

EXAMPLE 1

Two catalysts A and B were prepared, each comprising 0.6% by weight of platinum and 0.3% by weight of tin. The support was a Degussa silica with a specific surface area of 200 m² per gram.

Catalyst A (comparative)

Catalyst A was prepared using prior art techniques. The support was calcined at 500°C in a dry air for 5 hours then brought into contact with an ammoniacal solution (1N) for 15 hours, bubbling nitrogen through. Platinum was then deposited by introducing a solution of platinum tetramine hydroxide. The suspension was filtered, washed with distilled water and dried at 110°C in a stream of nitrogen. 10 grams of the solid containing 0.6% by weight of platinum was then reduced for 4 hours at 450°C in a stream of hydrogen. The catalyst was charged

under hydrogen into a reactor containing 300 cm³ of an aqueous ammoniacal solution (pH 11) containing 30 mg of tin in the form of tributyl tin acetate (Bu₃SnOC(O)CH₃). After 24 hours in contact in a hydrogen atmosphere, the reaction mixture was filtered, washed and dried at 80°C. The catalyst was reduced
5 in a stream of hydrogen at 550°C for 4 hours.

Catalyst B (in accordance with the invention)

Catalyst B was prepared from 10 grams of a solid containing 0.6% by weight of platinum, reduced at 450°C for 4 hours in a stream of hydrogen. The catalyst was then charged under hydrogen into a reactor containing 100 cm³ of an aqueous nitric
10 acid solution (pH 1) containing 30 mg of tin in the form of tributyltin acetate (Bu₃SnOC(O)CH₃). After 24 hours of contact under a hydrogen atmosphere, the reaction mixture was filtered, washed and dried at 80°C. The catalyst was reduced in a stream of hydrogen at 550°C for 4 hours.

Results

15 The solubility of the tributyltin acetate was substantially higher at a pH of 1 than at a pH of 11, enabling more concentrated aqueous tributyltin acetate solutions to be used. Thus the volume of aqueous solution used to prepare catalyst B in accordance with the invention was three times lower than that of catalyst A prepared in accordance with the prior art. Tin was thus deposited in smaller quantities of
20 aqueous solution, which represents a distinct advantage for the industrial preparation of these catalysts.

EXAMPLE 2

Catalysts A and B underwent an isobutane dehydrogenation test in an isothermal tube reactor. 1 g of catalyst was reduced at 550°C for 2 hours in a flow of
25 2 litres of hydrogen per hour. After injecting the feed, the temperature was

stabilised at 550°C. In-line analysis of the gaseous effluents was made by gas chromatography. The operating conditions were as follows:

- Feed: iC₄ N35 liquid air
- Temperature: 550°C
- 5 • Pressure: 0.1 MPa
- H₂/iC₄ (molar): 1
- Mass flow rate of liquid iC₄/catalyst mass 500 h⁻¹

The results obtained under these conditions are shown in Table 1.

TABLE 1

Catalysts	Duration (h)	Activity (moles.g Pt ⁻¹ s ⁻¹ .10 ⁻³)	Isobutene selectivity (% moles)
A	1	12.5	95.5
	3	12.2	96.0
	5	10.0	96.8
B	1	12.7	95.6
	3	12.2	95.8
	5	10.5	96.7

10

The performances of catalyst B prepared under the best conditions of solubility of the tin precursor were at least as good as those of catalyst A prepared in accordance with the prior art.

EXAMPLE 3

- 15 Five catalysts C, D, E, F and G were prepared, each comprising 0.6% by weight of platinum, 0.2% by weight of tin, 1% by weight of chlorine and 1% by weight of potassium with respect to the total catalyst weight. The support was a gamma alumina with a specific surface area of 200 m² per gram.

Catalyst C (comparative)

Catalyst C was prepared using prior art techniques. 150 cm³ of an aqueous solution of hydrochloric acid and stannic chloride containing 0.10 g of tin was added to 50 g of alumina support. It was left in contact for 3 hours then drained. The solid was then brought into contact with 150 cm³ of an aqueous hexachloroplatinic acid solution containing 0.3 g of platinum. It was left in contact for 3 hours, dried for 1 hour at 120°C then calcined for 2 hours at 500°C. 30 cm³ of an aqueous potassium carbonate solution containing 0.5 g of potassium was then added then the sample was dried at 120°C and calcined for 2 hours at 500°C.

Catalyst D (in accordance with the invention)

Catalyst D was prepared by impregnating tin before the platinum. 50 g of alumina support was brought into contact with 100 cm³ of an aqueous solution, at a pH of 8 by adding NH₃, containing 0.1 g of tin in the form of dimethyltin dichloride ((CH₃)₂SnCl₂). After reacting for 3 hours at ambient temperature, the solid was filtered then dried for 1 hour at 120°C and calcined at 500°C for 2 hours. 50 g of this solid was then brought into contact with 150 cm³ of an aqueous solution of hydrochloric acid and hexachloroplatinic acid containing 0.3 g of platinum. It was left in contact for 3 hours, dried for 1 hour at 120°C and calcined for 2 hours at 500°C. 30 cm³ of an aqueous potassium carbonate solution containing 0.5 g of potassium was added then the sample was dried at 120°C and calcined for 2 hours at 500°C.

Catalyst E (in accordance with the invention)

Catalyst E was prepared by co-impregnating platinum and tin. 50 g of alumina support was brought into contact with 30 cm³ of a solution containing 0.1 g of tin initially in the form of Me₃SnCl, 0.3 g of Pt in the form of hexachloroplatinic acid (H₂PtCl₆) and hydrochloric acid in a quantity such that the pH of the solution

was 1. The solid was dried for 1 hour at 120°C then calcined for 2 hours at 500°C. 30 cm³ of an aqueous potassium carbonate solution containing 0.5 g of potassium was then added and the sample was dried at 120°C then calcined for 2 hours at 500°C.

5 Catalyst F (in accordance with the invention)

Catalyst F was prepared from 50 g of alumina containing 0.6% by weight of platinum, reduced at 450°C in a hydrogen stream for 4 hours. After this reduction stage, the catalyst was charged, without ingress of air, into a reactor containing 100 cm³ of an aqueous Me₃SnCl solution at a pH of 4 containing a quantity of tin
10 required to deposit 0.2% by weight of tin on the support. After leaving in contact for 24 hours, the reaction mixture was filtered, washed then dried at 80°C. The catalyst was then dried for 1 hour at 120°C and calcined at 500°C for 2 hours. Potassium was then introduced by bringing 50 g of the catalyst into contact with 30 cm³ of an aqueous potassium carbonate solution containing 0.5 g of potassium; the sample was
15 then dried at 120°C and calcined for 2 hours at 500°C.

Catalyst G (in accordance with the invention)

Catalyst G was prepared by dry impregnation of tin and excess impregnation of platinum. 50 g of alumina support was brought into contact with 30 cm³ of an aqueous solution of trimethyltin chloride ((CH₃)₃SnCl) containing 0.1 g of tin. It
20 was left in contact for 3 hours then the solid was dried for 1 hour at 120°C and calcined at 500°C for two hours. The solid was brought into contact with 150 cm³ of an aqueous hexachloroplatinic acid solution containing 0.3 g of platinum. It was left in contact for 3 hours, dried at 120°C for 1 hour and calcined for 2 hours at 500°C. 30 cm³ of an aqueous potassium carbonate solution containing 0.5 g of potassium
25 was added and the sample was dried at 120°C then calcined for 2 hours at 500°C.

EXAMPLE 4

Catalysts C, D, E, F and G underwent an isobutane dehydrogenation test in an isothermal tube reactor. 1 g of catalyst was reduced at 550°C for 2 hours in a hydrogen flow of 2 litres per hour. After injecting the feed, the temperature was stabilised at 550°C. In-line analysis of the gaseous effluents was carried out by gas chromatography.

The operating conditions were as follows:

- Feed: iC_4 N35 liquid air
- Temperature: 550°C
- Pressure: 0.1 MPa
- H_2/iC_4 (molar): 1
- Mass flow rate of liquid iC_4 /catalyst mass: $725\ h^{-1}$

The results obtained under these conditions are shown in Table 2.

TABLE 2

Catalysts	Duration (h)	Activity (moles.g Pt ⁻¹ s ⁻¹ .10 ⁻³)	Isobutene selectivity (% moles)
C	1	17.1	99.0
	3	15.8	99.0
	5	15.1	99.2
D	1	18.9	99.2
	3	16.4	99.2
	5	15.6	99.4
E	1	18.1	99.1
	3	16.1	99.1
	5	15.2	99.3
F	1	20.2	99.0
	3	19.3	99.0
	5	18.9	99.2
G	1	19.3	99.0
	3	18.7	99.1
	5	17.9	99.1

The results show that the performances of catalysts D, E, F and G, prepared in accordance with the invention from an organometallic precursor of element M in an aqueous phase, were at least identical and even a little superior to those of catalyst C prepared in accordance with the prior art.

EXAMPLE 5

Three catalysts H, I and J were prepared, containing 0.4% by weight of platinum, 0.3% by weight of tin, 0.1% by weight of indium and 0.6% by weight of lithium. The support was a γ alumina with a specific surface area of 200 m² per gram.

Catalyst H (comparative)

Catalyst H was prepared using prior art techniques. 30 cm³ of an aqueous lithium acetate solution containing 0.3 g of lithium was added to 50 g of alumina support. It was left in contact for 3 hours then the solid was dried for 1 hour at 120°C and calcined at 350°C for two hours. The solid was brought into contact with 200 cm³ of an aqueous indium nitrate solution containing 0.05 g of indium. After leaving in contact for 3 hours, the solid was dried for 1 hour at 120°C and calcined for 2 hours at 530°C. The solid was then brought into contact with 30 cm³/g of an n-heptane solution containing 0.15 g of tin in the form of tetrabutyltin.

After leaving in contact for 3 hours, the solid was dried for 1 hour at 120°C and calcined for 2 hours at 530°C. Platinum was then introduced by adding 200 cm³ of a toluene solution containing 0.2 g of platinum in the form of platinum acetylacetonate. It was left in contact for 24 hours then dried for 1 hour at 120°C and calcined for 2 hours at 530°C.

Catalyst I (in accordance with the invention)

Catalyst I was prepared using the oil drop method. 0.88 g of tributyl tin acetate ($\text{C}_4\text{H}_9\text{SnOCOCCH}_3$) was introduced into 282 g of an aqueous 1.1% by weight nitric acid solution then 100 g of powdered boehmite was incorporated by stirring. The suspension was drained by passage through 1mm diameter calibrated tubes then coagulated by passage into a 3% by weight ammoniacal solution. The support beads formed were dried for 2 hours at 120°C and calcined for 2 hours at 600°C. 50 g of this solid was brought into contact with 30 cm³ of an aqueous lithium acetate solution containing 0.3 g of lithium. It was left in contact for 3 hours then the solid was dried for 1 hour at 120°C and calcined at 350°C for two hours. The solid was then brought into contact with 200 cm³ of an aqueous indium nitrate solution containing 0.05 g of indium. After leaving in contact for 3 hours, the solid was dried for 1 hour at 120°C and calcined for 2 hours at 530°C. Platinum was introduced by adding 200 cm³ of a toluene solution containing 0.2 g of platinum in the form of platinum acetylacetonate. It was left in contact for 24 hours then dried for 1 hour at 120°C and calcined for 2 hours at 530°C.

Catalyst J (in accordance with the invention)

Catalyst J was prepared using the sol-gel method. The support was prepared by hydrolysis of an aluminium isopropylate solution $\text{Al}(\text{OiPr})_3$ in isopropanol using an aqueous trimethyltin chloride ($(\text{CH}_3)_3\text{SnCl}$) solution at a pH of 4, followed by a heat treatment at 450°C. Lithium was then introduced by bringing 50 g of this support into contact with 30 cm³ of an aqueous lithium acetate solution containing 0.3 g of lithium. It was left in contact for 3 hours then the solid was dried for 1 hour at 120°C and calcined at 350°C for two hours. The solid was brought into contact with 200 cm³ of an aqueous indium nitrate solution containing 0.05 g of indium. After leaving in contact for 3 hours, the solid was dried for 1 hour at 120°C and

calcined for 2 hours at 530°C. Finally, platinum was introduced by adding 200 cm³ of a toluene solution containing 0.2 g of platinum in the form of platinum acetylacetonate. It was left in contact for 24 hours than dried for 1 hour at 120°C and calcined for 2 hours at 530°C.

EXAMPLE 6

Catalysts H, I and J underwent a n-dodecane dehydrogenation test in an isothermal tube reactor. 2 g of catalyst was reduced at 450°C for 2 hours in a hydrogen flow of 4 litres per hour. The operating conditions were as follows:

- Feed: n-dodecane
- Temperature: 450°C or 470°C
- Pressure: 0.2 MPa
- H₂/nC₁₂ (molar): 5
- Mass flow rate of liquid nC₁₂/catalyst mass 80 h⁻¹

The results obtained under these conditions are shown in Table 3. The nC₁₂ conversions and yields are expressed as a % by weight with respect to the feed.

TABLE 3

Catalyst	Temperature (°C)	nC ₁₂ conversion (%)	Yields (%)	
			nC ₁₂ olefins	Aromatics
H	450	10.4	9.6	0.3
	470	13.5	12.1	0.7
	450	9.0	8.2	0.1
I	450	10.5	9.9	0.2
	470	14.8	12.8	0.7
	450	9.6	8.6	0.2
J	450	10.6	9.9	0.2
	470	14.8	13.1	0.6
	450	10.2	9.2	0.2

The olefin yields of catalysts I and J, prepared in accordance with the invention in an aqueous medium from organometallic Sn precursors which were at least identical to those for catalyst H prepared in accordance with the prior art.

B. PREPARATION OF CATALYSTS AND THEIR USE IN ISOPRENE 5 HYDROGENATION

EXAMPLE 7

Four catalysts K, L, M and N were prepared containing 0.4% by weight of palladium and 0.4% by weight of tin. The support was an alumina with an specific surface area of 70 m² per gram.

10 Catalyst K (comparative)

Catalyst K was prepared using prior art techniques. 40 cm³ of an aqueous palladium nitrate solution was added to 50 g of alumina support. The catalyst was dried at 110°C and calcined at 450°C in air then reduced at 450°C in a stream of hydrogen. The catalyst was then charged without ingress of air into a reactor
15 containing toluene. The required quantity of tetrabutyl tin was then injected at 20°C to deposit 0.4% by weight of tin on the support. After 24 hours under these conditions, the catalyst was filtered, washed, dried and reduced at 450°C.

Catalyst L (comparative)

Catalyst L was prepared using prior art techniques. Palladium was deposited
20 by bringing the alumina support into contact with a palladium nitrate solution. The catalyst was dried at 110°C and calcined at 450°C in air then reduced at 450°C in a stream of hydrogen. 10 g of the catalyst was then charged, without ingress of air, into a reactor containing 400 cm³/g of an ammoniacal solution (pH 10.5) containing 40 mg of tin in the form of tributyltin acetate (Bu₃SnOC(O)CH₃). The pressure was

then raised to 4 MPa and the temperature to 100°C. After 1 hour under these conditions, the reaction mixture was filtered, washed, dried and reduced at 450°C.

Catalyst M (in accordance with the invention)

Catalyst M was prepared from 10 grams of solid containing 0.4% by weight
 5 of palladium reduced at 450°C in a stream of hydrogen for 4 hours. This catalyst
 was charged, without ingress of air, into a reactor containing 150 cm³ of a nitric acid
 solution (pH 1) containing 40 mg of tin in the form of tributyltin acetate
 (Bu₃SnOC(O)CH₃). The pressure was then raised to 4 MPa and the temperature was
 raised to 100°C. After 1 hour under these conditions, the reaction mixture was
 10 filtered, washed, dried and reduced at 450°C.

Catalyst N (in accordance with the invention)

For catalyst N, a quantity of 50 g of alumina support was brought into contact
 with 40 cm³ of an aqueous palladium nitrate solution. The catalyst was then dried at
 110°C, calcined in air at 450°C and reduced at 450°C in a stream of hydrogen. After
 15 this reduction step, 50 g of this catalyst containing 0.4% of palladium was charged,
 without ingress of air, into a reactor containing 150 cm³ of an aqueous solution of
 Me₃SnCl (pH=4) containing the quantity of tin required to deposit 0.4% by weight
 of tin on the support. After leaving in contact for 24 hours, the reaction mixture was
 filtered, washed then dried at 80°C.

20

EXAMPLE 8

The catalysts were then tested in an isoprene hydrogenation reaction in a
 perfectly stirred reactor under the following operating conditions:

- Feed: n-heptane + isoprene
- Temperature: 65°C
- 25 • Pressure: 1 MPa

The results obtained under these conditions are shown in the table. The yields are expressed in mole % after 1 hour of operation.

Catalysts	Conversion (%)	Selectivity (%)	
		Iso-paraffins	Iso-olefins
K	100	8	92
L	100	6	94
M	100	6	94
N	100	5	95

5 The solubility of the tributyltin acetate was substantially higher at a pH of 1 than at a pH of 11, enabling more concentrated aqueous tributyltin acetate solutions to be used. Thus the volume of aqueous solution used to prepare catalyst M in accordance with the invention was 2.5 times lower than that of catalyst L prepared in accordance with the prior art. The tin was thus deposited using lower quantities of
 10 aqueous solution, which is a distinct advantage when preparing these catalysts on an industrial scale.

The performances of catalysts M and N, prepared in accordance with the invention in an aqueous medium from an organometallic precursor, were close to or even slightly better than those of catalysts K and L prepared using prior art methods,
 15 with the advantage of preparation in an aqueous medium with better solubilities of the tin precursors than for the prior art preparations.

C. PREPARATION OF CATALYSTS AND THEIR USE IN HYDROCARBON CONVERSIONS

EXAMPLE 9

Nine catalysts P, Q, R, S, T, U, V, W and X were prepared, comprising 0.4% by weight of platinum, 0.25% by weight of tin and 1.2% by weight of chlorine. The support was a gamma alumina with a specific surface area of 200 m² per gram.

5 Catalyst P (comparative)

Catalyst P was prepared using prior art techniques. The support was a γ alumina with a specific surface area of 210 m² per gram. 150 cm³ of an aqueous solution of hydrochloric acid and stannic chloride containing 0.125 g of tin was added to 50 g of alumina support. It was left in contact for 3 hours then drained.
10 The solid was then brought into contact with 150 cm³ of an aqueous solution of hexachloroplatinic acid containing 0.2 g of platinum. It was left in contact for 3 hours, dried for 1 hour at 120°C then calcined for 2 hours at 500°C.

Catalyst Q (comparative)

Catalyst Q was prepared using prior art techniques. 10 g of alumina support
15 was brought into contact with 250 cm³ of an aqueous ammoniacal solution (pH 11) containing 0.025 g of tin in the form of tributyltin acetate, Bu₃SnOC(O)CH₃. After 3 hours of reaction at ambient temperature, the solid was filtered, dried for 1 hour at 120°C then calcined at 500°C for 2 hours. 10 g of this solid was then brought into contact with 100 cm³ of an aqueous solution of hydrochloric acid and
20 hexachloroplatinic acid containing 0.04 g of platinum. It was left in contact for 3 hours then dried for 1 hour at 120°C and calcined for 2 hours at 500°C.

Catalyst R (in accordance with the invention)

A quantity of 10 g of alumina support was brought into contact with 100 cm³ of an aqueous ammoniacal solution (pH 1) containing 0.025 g of tin in the form of
25 tributyl tin acetate Bu₃SnOC(O)CH₃. After reacting for 3 hours at ambient

temperature, the solid was filtered, dried for 1 hour at 120°C and calcined at 500°C for 2 hours. 10 g of this solid was brought into contact with 100 cm³ of an aqueous solution of hydrochloric acid and hexachloroplatinic acid containing 0.04 g of platinum. It was left in contact for 3 hours, dried for 1 hour at 120°C then calcined
 5 for 2 hours at 500°C.

Catalyst S (in accordance with the invention)

Catalyst S was prepared by bringing 50 g of alumina support into contact with 150 cm³ of an aqueous solution, at a pH of 8, by adding NH₃, containing 0.125 g of tin in the form of dimethyl tin dichloride ((CH₃)₂SnCl₂). After reacting for 3
 10 hours at ambient temperature, the solid was filtered, dried for 1 hour at 120°C and calcined at 500°C for 2 hours. 50 g of this solid was brought into contact with 150 cm³ of an aqueous solution of hydrochloric acid and hexachloroplatinic acid containing 0.2 g of platinum. It was left in contact for 3 hours, dried for 1 hour at 120°C then calcined for 2 hours at 500°C.

15 Catalyst T (in accordance with the invention)

Catalyst T was prepared by bringing 50 g of an alumina support into contact with 30 cm³ of a hydrochloric acid solution (pH = 1) containing 0.125 g of tin initially in the form of Me₃SnCl and 0.2 g of Pt in the form of hexachloroplatinic acid (H₂PtCl₆). The solid was then dried for 1 hour at 120°C and calcined for 2
 20 hours at 500°C.

Catalyst U (in accordance with the invention)

Catalyst U was prepared using the oil drop method. 0.56 g of tributyl tin acetate (C₄H₉)₃SnOC(O)CH₃ was introduced into 282 g of an aqueous 1.1% by weight nitric acid solution then 100 g of powdered boehmite was incorporated by
 25 stirring. The suspension was drained by passage through calibrated 1mm diameter

tubes then coagulated by passage into a 3% by weight ammoniacal solution. The support beads formed were dried for 2 hours at 120°C and calcined for 2 hours at 600°C. 50 g of this solid was brought into contact with 150 cm³ of an aqueous hexachloroplatinic acid solution containing 0.2 g of platinum. It was left in contact
5 for 3 hours then dried for 1 hour at 120°C and calcined at 500°C for two hours.

Catalyst V (in accordance with the invention)

A catalyst V was prepared from 50 g of a solid containing 0.4% by weight of platinum, reduced at 450°C in a stream of hydrogen for 4 hours. The platinum had been deposited on the alumina support by bringing it into contact with 150 cm³ of an
10 aqueous hexachloroplatinic acid solution containing 0.2 g of platinum. The solid was dried for 1 hour at 120°C, then reduced for 2 hours at 450°C. The catalyst was charged, without ingress of air, into a reactor containing 200 cm³ of an aqueous trimethyl tin chloride solution (CH₃)₃SnCl at a pH of 1, containing a quantity of tin sufficient to deposit 0.2% by weight of tin on the support. After 24 hours of contact,
15 the reaction mixture was filtered, washed, dried at 80°C and calcined for 2 hours at 500°C.

Catalyst W (in accordance with the invention)

30 cm³ of an aqueous solution of trimethyltin chloride (CH₃)₃SnCl at a pH of 4 containing 0.125 g of tin was added to 50 g of alumina support. It was left in
20 contact for 3 hours then the solid was dried for 1 hour and calcined at 500°C for 2 hours. Platinum was then deposited by excess impregnation with a hexachloroplatinic acid solution to a 0.4% by weight platinum content with respect to the calcined support. After calcining at 450°C for a period of 12 hours, the catalyst was reduced in hydrogen at 500°C for 4 hours.

25 Catalyst X (in accordance with the invention)

Catalyst X was prepared using the sol-gel method. The support was prepared by hydrolysis of a solution of aluminium isopropylate $\text{Al}(\text{OiPr})_3$ in isopropanol using an aqueous solution of trimethyltin chloride $(\text{CH}_3)_3\text{SnCl}$ at a pH of 4, followed by heat treatment at 450°C . Platinum was then deposited by excess impregnation with a
 5 hexachloroplatinic acid solution to a 0.4% by weight platinum content with respect to the calcined support. After calcining at 450°C for a period of 12 hours, the catalyst was reduced in a stream of hydrogen at 500°C for 4 hours.

EXAMPLE 10

Samples of these catalysts prepared as described above were tested by
 10 transforming a feed with the following characteristics:

Density at 20°C	0.753 kg/dm^3
Research octane number	~ 60
Paraffin content	49.4% by volume
Naphthene content	35.1% by volume
15 Aromatics content	15.5% by volume

Transformation was carried out in the presence of hydrogen under the following operating conditions:

Temperature	490°C
Total pressure	0.30 MPa
20 Feed flow rate	2.0 kg per kg of catalyst per hour

Before injecting the feed, the catalysts were activated at 450°C in hydrogen for 2 hours. The performances obtained after 24 hours of operation are shown in the table below.

Catalyst	Reformate yield (wt %)	Research octane number	Aromatics yield (wt %)	C ₄ yield (wt %)
P (comparative)	92.3	99.2	68.6	4.3
Q (comparative)	92.4	100.3	70.32	4.2
R	91.9	100.7	71.28	4.0
S	92.0	101.0	71.96	4.4
T	92.8	99.7	70.07	3.7
U	92.3	100.1	70.42	3.9
V	92.2	101.3	73.10	4.1
W	91.7	101.7	73.27	4.4
X	91.9	101.4	72.85	4.5

The performances of catalysts R, S, T, U, V, W and X prepared in accordance with the invention in an aqueous medium from an organometallic precursor either by impregnating the support with the compounds Me_3SnCl , Me_2SnCl_2 or $\text{Bu}_3\text{SnOC}(\text{O})\text{CH}_3$ or by introducing tributyltin acetate when forming the support were better than that of catalyst P prepared using prior art techniques.

Further, the solubility of tributyltin acetate was substantially higher at a pH of 1 than at a pH of 11, enabling more concentrated tributyltin acetate solutions to be used. Thus the volume of aqueous solution used in preparing catalyst R in accordance with the invention was 2.5 times lower than that of catalyst Q prepared in accordance with the prior art. Tin was thus deposited in lower quantities of aqueous solution, which constitutes a distinct advantage when preparing these catalysts on an industrial scale. Further, the performances of catalyst R prepared under the better tin precursor solubility conditions were at least as good if not better than that of catalyst Q prepared in accordance with the prior art.

CLAIMS

1. A process for preparing a catalyst comprising at least one support, at least one binder, at least one metal from group VIII of the periodic table and at least one additional element M selected from germanium, tin, lead, rhenium, niobium, gallium, indium, thallium, gold and silver, in which said additional element M is introduced in an aqueous solvent at a pH of about less than 10, said additional element M being in the form of at least one hydrosoluble organometallic compound comprising at least one carbon-M bond.
2. A process according to claim 1, in which the pH of the aqueous solution of additional element M is less than 10.
3. A process according to claim 1 or claim 2, in which at least one alkali or alkaline-earth metal is also introduced into the catalyst.
4. A process according to any one of claims 1 to 3, in which at least one metalloid is also introduced into the catalyst.
5. A process according to any one of claims 1 to 4, in which at least one halogen or a halogenated compound is also introduced into the catalyst.
6. A process according to any one of claims 1 to 5, in which the group VIII metal is selected from iridium, nickel, palladium, platinum, rhodium and ruthenium.

7. A process according to any one of claims 1 to 6, in which the additional element M introduced in the organometallic form is selected from germanium and tin.
- 5 8. A process according to any one of claims 1 to 7, in which a further at least one element M is introduced.
- 10 9. A process according to any one of claims 1 to 8, in which the precursor of additional element M is selected from polyalkyl halides, polyalkyl hydroxides, polyalkyl oxides, polyalkyl carboxylates, polyalkyl carbonates, polyalkyl nitrates, polyalkyl sulphates, compounds with general formula $(R1)_xM(R2)_y(R3)_z$ where $x+y+z$ = the valency of metal M and where R1 is selected from alkyl, cycloalkyl, nitrile (CN), carbonyl (CO), aryl, alkylaryl and arylalkyl functions, where R2 is a function with formula $C_aH_bR'_c$, where 15 R' represents a hydroxide, halide carboxylate, PO_3H or SO_3H function and where R3 is an aquo, oxo (MO), alkoxide (O-alkyl), hydride, hydroxyl, alkylsulphonate, alkylsulphate, thioalkyl, $N(SO_3R'')_2$, PR''_2 or PR''_3 group where R'' is an alkyl group.
- 20 10. A process according to claim 9, in which at least one alkyl group is replaced by an alkenyl or aryl group.
- 25 11. A process according to any one of claims 1 to 10, in which the additional element M is introduced during synthesis of the support using a sol-gel type technique.

12. A process according to any one of claims 1 to 10, in which the additional element M is introduced into an alumina hydrosol in the form of an organometallic compound in a solution with a pH in the range 0 to 10.
13. A process according to any one of claims 1 to 10, in which additional element M is introduced using an oil drop method.
14. A process according to claim 13, in which the organometallic compound of element M is selected from polyalkyl acetates, polyalkyl oxides, polyalkyl carbonates, polyalkyl carboxylates, polyalkyl sulphates, compounds with general formula $(R1)_xM(R2)_y(R3)_z$ where $x+y+z$ = the valency of metal M and where R1 is selected from the alkyl, cycloalkyl, nitrile (CN), carbonyl (CO), aryl, alkylaryl and arylalkyl functions, where R2 is a function with formula C_4H_6R' , where R' represents a hydroxyide, carboxylate, PO_3H or SO_3H function and where R3 is an aquo, oxo (MO), alkoxide (O-alkyl), hydride, hydroxyl, alkylsulphonate, alkylsulphate, thioalkyl, $N(SO_3R'')_2$, PR''_2 or PR''_3 group where R'' is an alkyl group.
15. A process according to any one of claims 1 to 10, in which the group VIII metal, additional element M in the organometallic form in an aqueous solvent with a pH of less than 10, optional halogen, optional alkali or alkaline-earth metal, optional metalloid, and optional other element M are introduced by simultaneous or successive support impregnation steps.

16. A process according to claim 15, in which a support is impregnated using an aqueous or organic solution of at least one group VIII metal, filtered, dried, calcined in air, and reduced in hydrogen; and the product obtained is impregnated with an aqueous solution with a pH of less than 10 of an organometallic compound of additional element M, filtered, dried, optionally reduced, then calcined.

17. A process according to claim 15, in which a support is impregnated with an aqueous solution of an organometallic compound of additional element M with a pH of less than 10, dried, calcined and the solid obtained is impregnated with an aqueous or organic solution of at least one group VIII metal, dried and calcined.

18. A process according to claim 17, in which the organometallic compound of additional element M is a polyalkyl halide compound of M or a polyalkyl oxide compound of M.

19. A process according to claim 18, in which the organometallic compound of additional element M is a trimethyl halide of M or a dimethyl dihalide of M.

20. A catalyst prepared according to the process of any one of claims 1 to 19.

21. Use of a catalyst according to claim 20 or prepared according to the process any one of claims 1 to 19 in organic compound transformation reactions.

22. Use of a catalyst according to claim 21 in reactions for dehydrogenating saturated aliphatic hydrocarbons to the corresponding olefinic hydrocarbons.
23. Use according to claim 22 at a temperature of 400°C to 800°C at a pressure of 0.02 to 2 MPa, with a mass flow rate of treated feed per unit mass of catalyst of 0.5 to 100 kg/kg/hour, and with a hydrogen/hydrocarbon mole ratio of 0 to 20.
24. Use of a catalyst according to claim 21 in catalytic hydroreforming and aromatic compound production reactions.
25. Use according to claim 24, in which the feed is brought into contact with the catalyst at a temperature in the range 400°C to 7000°C with a treated feed mass flow rate per unit mass of catalyst in the range 0.1 to 10 g/kg/h, at a pressure in the range from atmospheric pressure to 4 MPa.
26. Use according to claim 24 or claim 25, in which at least a portion of the hydrogen produced is recycled in a molar recycle ratio in the range 0.1 to 10.
27. Use according to any one of claims 24 to 26, in which the feed is constituted by paraffinic, naphthenic and aromatic hydrocarbons containing 5 to 12 carbon atoms per molecule.
28. Use of a catalyst according to claim 21, in reactions for selective hydrogenation of unsaturated compounds such as acetylenes or diolefins.

29. Use according to claim 28 in which in the catalyst, the group VIII metal is selected from nickel, palladium, platinum, rhodium, ruthenium and iridium, preferably platinum, palladium and nickel.
- 5 30. Use according to claim 28 or 29, in which in the catalyst, additional element M is selected from germanium, tin, silver and gold.
- 10 31. Use according to any one of claims 28 to 30 in which in the catalyst, the precursor of additional element M is selected from carboxylates of organic compounds of additional element M.
- 15 32. Use according to any one of claims 28 to 31 in a process in which the feed to be treated is brought into contact with the catalyst at a pressure in the range from atmospheric pressure to 6 MPa and at a temperature in the range 20°C to 200°C with a mass flow rate of treated feed per unit mass of catalyst in the range from 0.1 to 10 kg/kg/h.
- 20 33. Use according to any one of claims 28 to 32, in which the feeds to be treated are C2 or C3 steam cracking cuts.
34. Use according to any one of claims 28 to 33, in which the feed to be treated is a C4 steam cracking cut.
- 25 35. Use according to any one of claims 28 to 34, in which the feeds to be treated are C5-C8 steam cracking gasoline cuts.

36. Use according to any one of claims 28 to 35, in which the feed to be treated is a C3 catalytic cracking cut.
- 5 37. Use according to any one of claims 28 to 36, in which the feed to be treated is a C4 catalytic cracking cut.
38. Use according to any one of claims 28 to 37, in which the feeds to be treated are C5-C8 catalytic cracking cuts.
- 10 39. A process according to claim 1 substantially as hereinbefore described with reference to the accompanying examples.
40. A catalyst according to claim 20 substantially as hereinbefore described with
15 reference to the accompanying examples.
41. Use of a catalyst according to claim 21 substantially as hereinbefore described with reference to the accompanying examples.



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Claims searched: 1-41

Examiner: Dr Albert Mthupha
Date of search: 22 December 2000

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Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

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Other: ONLINE: EPODOC, JAPIO, WPI.

Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevant to claims
X	US 4548918 A SOCIETE FRANCAISE, see Example 1.	1 at least.
X	US 3531543 A CLIPPINGER et al, see whole document, note Examples 1-4.	1 at least.

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
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